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13. ABSTRACT (Maximum 200 words)

The goal of this project was to evaluate the potential of supercritical extraction (SCE) for producing a high-quality mesophase suitable for conversion into high-performance carbon fibers with excellent thermal and/or mechanical properties. Mesophase pitch fractions were produced by fractionation of an isotropic pitch with supercritical toluene in a region of liquid-liquid equilibrium. Results indicate that SCE provides greater product flexibility and uses less solvent than conventional solvent extraction. In particular, several 100% mesophase fractions with significantly different yields, softening points, and chemical compositions were made.

Selected supercritically extracted mesophase fractions were melt-spun into both round and ribbon-shaped fibers. To facilitate the evaluation of these mesophases, a new method (i.e., Z-values by WAXD) was investigated for predicting the properties of final fibers from those of as-spun fibers. Lower Z-values of as-spun fibers yielded, upon identical heat treatment, improvements in tensile properties, crystallographic parameters, and thermal conductivities for the associated final fibers. Even though the heat treatment of the as-spun fibers was not optimized, final fibers with thermal conductivities equal to Amoco's P-120 fibers were produced by graphitizing at only 2400 °C. Finally, a preliminary design analysis indicates that producing mesophase by SCE is economically competitive with today's best commercial processes.

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Supercritical Fluid Extraction for High Thermal Conductivity Carbon Fibers

1. Foreword

The performance of many weapon and electronic systems is limited by their ability to dissipate heat. For example, during high-speed maneuvers aerodynamic drag generates significant heat in the skin of aircraft and missiles. Perhaps more importantly, the increasing concentration of electronics makes the buildup of electrically generated heat a severe problem in modern weapon systems.

High thermal conductivity carbon fibers that have up to three times the thermal conductivity of copper can be used to eliminate these thermal buildup problems and quickly dissipate excess heat. Unfortunately, these particular pitch-based fibers are very expensive (i.e., about \$3000/kg). A significant part of the problem is quality of the starting fiber precursor material, which is a carbonaceous mesophase. Fibers produced from conventional mesophase must be heat-treated to very high heat treatment temperatures (~3000 °C) to generate the desired extended graphitic crystallinity, adding significantly to product cost. As a result, high thermal conductivity carbon fibers are ~10 times more expensive than other pitch-based carbon fibers, making them impractical for high-volume applications.

In this project, a supercritical extraction process was evaluated for the production of refined meosphase pitches. The expectation was that a higher-quality mesophase could be melt-spun into a fiber with greatly improved as-spun orientation, and that this highly oriented fiber could develop excellent thermal and mechanical properties at much lower (i.e., ~2500 °C) heat treatment temperatures.

Supercritical Fluid Extraction for High Thermal Conductivity Carbon Fibers

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4. Statement of the Problem

The goal of this project was to evaluate the potential of supercritical extraction for producing a high-quality mesophase suitable for conversion into high-performance carbon fibers with excellent mechanical and/or thermal properties. An additional issue to be resolved was whether such a supercritical extraction process for producing mesophase would be economically feasible on a commercial scale. The research plan that was carried out to accomplish these goals, and the results that were obtained, are described below.

5. Results and Accomplishments

a. Computer Control of the Supercritical Extraction Apparatus. Before discussing the automation work, a brief description of the apparatus and its operation follows for completeness. A more detailed discussion can be found elsewhere [1,2]. The apparatus (see Figure 1) is of the continuous-flow (versus batch) type both for improved product consistency and so that the relatively large samples of mesophase required for carbon fiber manufacture can be more easily produced. For a typical experiment, petroleum pitch is pumped indirectly using either of two high pressure cylinders mounted in parallel. Each of these cylinders contains a floating piston, which is moved by the working fluid toluene. The supercritical solvent, which is toluene, is pumped independently at a predetermined flow rate to obtain a specified solvent-to-pitch (S/P) ratio. The two streams are preheated and then combined in an impingement mixer followed by a mixing coil before reaching an equilibrium cell, which functions as a phase separator. The preheating, mixing, and separation steps are performed in an isothermal nitrogen bath. At the operating conditions of temperature, pressure, and S/P ratio selected for this work, two liquid phases are formed. The heavy and light liquid phases are collected independently through bottom and top ports exiting the separator, respectively. The interface in the equilibrium cell is monitored by an electrical AC impedance technique [3]. The system pressure is controlled by the top-phase valve, and the bottom-phase valve is used for level control in the cell. After expansion to atmospheric pressure, both samples are collected. The top phase is mainly toluene (about 80 wt %) and contains the lower molecular weight, isotropic portion of the pitch. In contrast, the bottom phase consists of only about 20 wt % toluene and contains the higher molecular weight, mesophase-containing portion of the pitch. The bottom phase is then dried under vacuum to eliminate any residual toluene. The resulting bottom phase is a solid at ambient temperature and consists of up to 100 % mesophase.

Working in collaboration with process control experts in the Department of Chemical Engineering at Clemson, we automated the apparatus described above. A Pentium computer-based control system was designed, developed, and subsequently used to control the extraction pressure, collect top- and bottom-phase samples, and log in the experimental data. Microsoft Visual Basic® was used to create the software that runs the system. The metering valves that are used for pressure regulation, control of the liquid level in the phase separator, and sample collection are now manipulated using a servo motion control system. The dramatic improvements in both pressure control and in the control of the interface level in the phase separator are shown in Figures 2 and 3. Additional details of the apparatus construction and operation are given elsewhere [2,4].

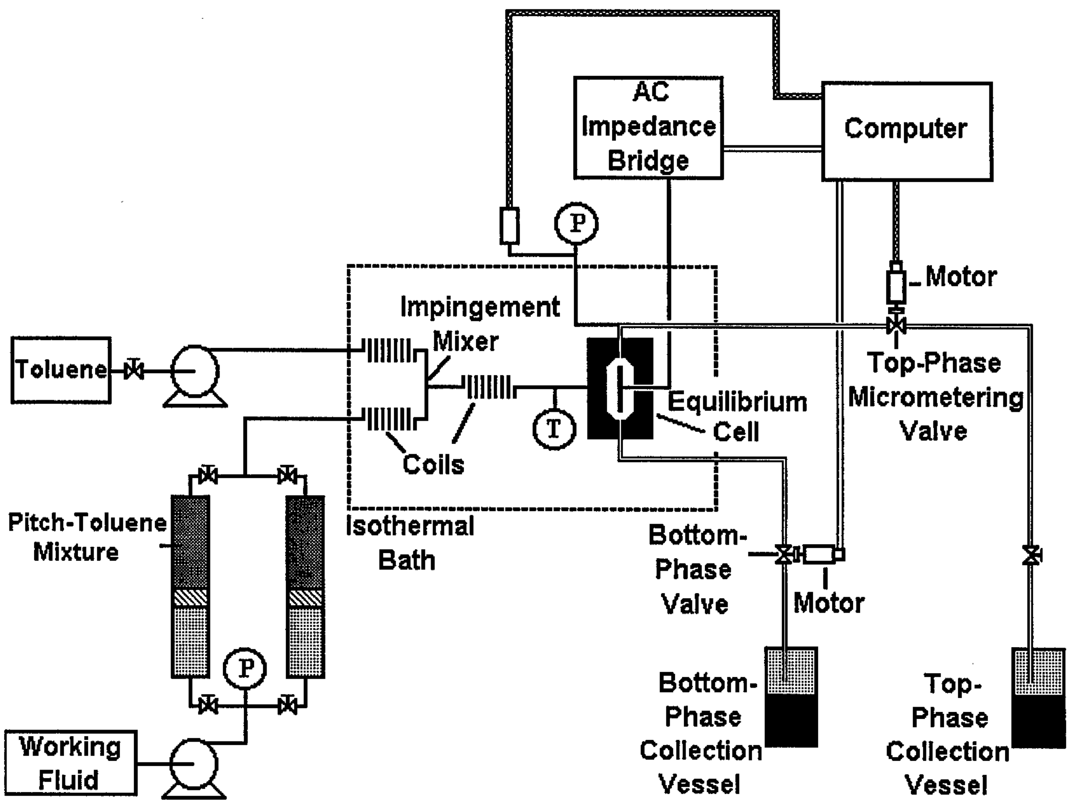

Figure 1. Schematic of the supercritical fluid extraction apparatus.

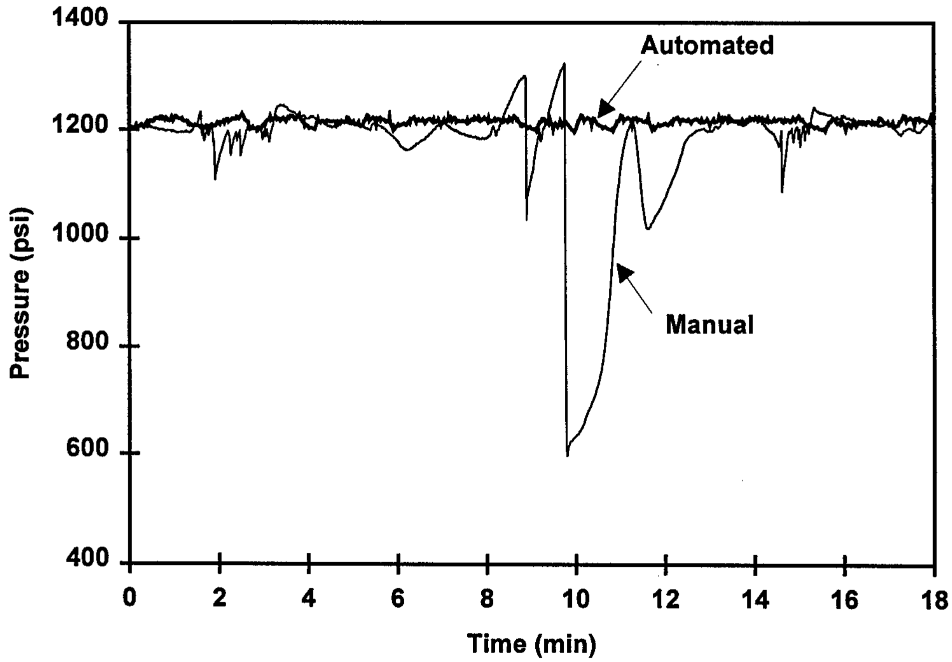

Figure 2. Typical pressure control during manual and semiautomated control of the apparatus.

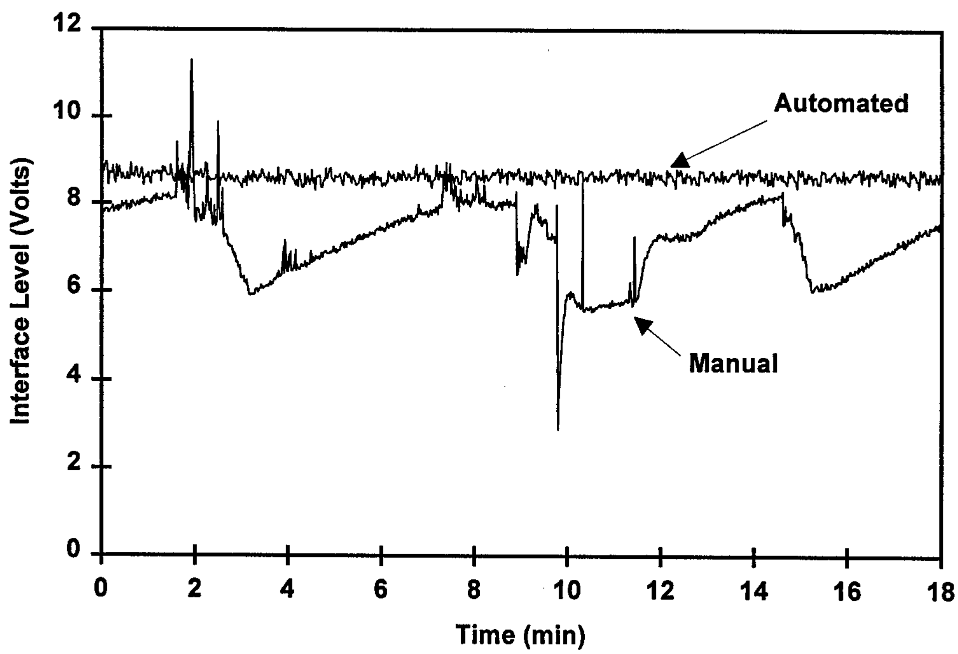

Figure 3. Typical interface level behavior during manual and semiautomated control of the apparatus.

The control system has now been in use on a continuous basis since late 1995 and has demonstrated its usefulness in several ways. First, only one student is now required to run the apparatus; previously two were required. Second, more reproducible samples are being produced with the control scheme. Third, we can, for the first time, produce the relatively large amounts of mesophase required for fiber testing. For example, during one busy 6-month period, approximately 2 kg of mesophase were produced. Before automating the apparatus, no more than about one-tenth that amount had been made in a comparable time period.

b. *Production of Mesophase Pitches by Supercritical Extraction.* In early exploratory work, Clemson researchers had shown that the properties of mesophase fractions produced by supercritical extraction with toluene could be altered by varying the operating temperature, pressure, and solvent-to-pitch (S/P) ratio [3]. In this project, an organized experimental exploration was performed to help us understand (1) how mesophase pitch properties can be modified and controlled by supercritical extraction, and (2) how sensitive mesophase properties are to processing variables. The exploration was performed according to the principles of the statistical design of experiments. In particular, the central composite design of Box and Wilson [5] was used to explore the effects of extraction temperature, solvent solubility parameter, and S/P ratio on the properties of the mesophase fractions produced.

Results of the experimental design were successful in producing mesophase pitches with a range of chemical and physical properties. In fact, six of the nine pitch fractions contained 100% mesophase and had a range of softening points. (100% mesophase fractions are of particular interest for the manufacture of carbon artifacts.) The operating conditions used to produce these six fractions (designated as M1-M6), the product yields, and the solvent compositions of the top and bottom phases are given in Table I.

Table I. Mesophase Pitch Fractions Produced by Supercritical Extraction

	Operating Conditions			Toluene Mass Fraction		Product Yield[b]
	T (°C)	P (δ^b)[a] (bar)	S/P Ratio	Bottom Phase	Top Phase	
M1	340	84 (4.3)	3.0	0.226	0.800	0.261
M2	320	94 (5.0)	3.5	0.211	0.805	0.164
M3	310	94 (5.3)	3.0	0.214	0.771	0.119
M4	310	94 (5.3)	4.0	0.184	0.821	0.128
M5	320	94(5.0)	4.5	0.181	0.847	0.135
M6	330	155 (5.3)	4.0	0.171	0.814	0.092

[a] Solvent solubility parameter in $(cal/cc)^{1/2}$.
[b] Product yield = fraction of feed pitch recovered as mesophase in the bottom phase.

Several physical and chemical properties of the meosphase pitch fractions are given below in Table II. Molecular weight distributions of the fractions were obtained by gel permeation chromatography (GPC), and the chemical compositions of the mesophases were studied by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Specifically, DRIFTS was used to monitor the average size of the aromatic ring structures in the mesophases (referred to as the ortho-substitution index (OSI)) [6], the extent to which these aromatic rings are substituted with alkyl groups (referred to as the C-H substitution index (CHSI)) [6], and the extent to which naphthenic molecules are substituted with alkyl groups (referred to as the alkyl-substitution index (AI)) [7].

Table II. Properties of the Feed Pitch and of the Mesophase Pitch Fractions

	SP[a] (°C)	Meso[b] (%)	M_W[c]	I_{OS}[d]	I_{CH}[e]	I_A[f]	C/H[g]
Feed Pitch	103	0	1020	0.317	0.572	0.487	1.48
M1	233	90	1440	0.275	0.473	0.405	1.81
M2	269	100	1550	0.266	0.474	0.425	2.04
M3	272	100	1580	0.253	0.466	0.427	2.00
M4	303	100	1620	0.259	0.502	0.464	2.10
M5	299	100	1590	0.263	0.464	0.425	1.91
M6	323	100	1670	0.247	0.461	0.416	2.17

[a] Softening point.
[b] Percent mesophase by polarized light microscopy.
[c] Weight average molecular weight by GPC.
[d] Ortho-substitution index by DRIFTS.
[e] C-H substitution index by DRIFTS.
[f] Alkyl-substitution index by DRIFTS.
[g] C/H ratio by elemental analysis.

The results in Tables I and II indicate that supercritical extraction can be used to produce mesophase pitches with significantly different yields and softening points. Furthermore, the C/H ratio and DRIFTS results presented in Table II indicate that fractions can differ significantly in their chemical composition (for example, compare alkyl substitution values for M1 and M4). The ability to control the degree of alkyl substitution in mesophases is important for oxidative stabilization, because the alkyl groups are the reactive sites for oxygen molecules [8].

In summary, the results of the above experimental investigation, which are presented in more detail elsewhere [1], indicate that supercritical extraction has several advantages compared to conventional solvent extraction, including (1) lower solvent requirements and (2) product flexibility with the use of a single, inexpensive solvent.

c. As-spun Orientation as an Indication of Final Fiber Properties. As demonstrated above, an attractive feature of supercritical extraction is that one can produce mesophase pitches with a wide range of properties, and thus in principle produce the best mesophase for high thermal conductivity carbon fibers. However, the time required to evaluate many different mesophases by conventional means (i.e., to optimize the melt-spinning temperature for each mesophase, oxidize and graphitize the as-spun fibers, and then measure final fiber properties) is prohibitive. We therefore investigated a technique for predicting final fiber properties from as-spun fibers in an efficient, cost-effective manner. The technique uses wide angle X-ray diffraction (WAXD) to monitor the degree of misorientation present in the aromatic layers of as-spun fibers with respect to the fiber axis. This misorientation is known as the Z-value, and was proposed by us to be a function of the misorientation (or Z-value) present in the graphene layers of final carbon fibers with respect to the fiber axis. Low Z-values are desirable because perfectly oriented graphene layers (in conjunction with large crystallite sizes) lead to fibers with very high thermal conductivities.

For this study, the M2 mesophase was selected for testing. A number of fiber sets were melt-spun; three of these sets were chosen for further testing (see Table III). These three fiber sets were referred to as A, B, and C. Considering the as-spun Z-values that were obtained, the degree of misorientation decreases from A to B, and the as-spun Z-values of B and C are similar, with the orientation of C being slightly better than that of B. This indicates that the molecular orientation that occurs in the capillary increased as the spin temperature increased from 346 °C to 354 °C. Therefore, if our premise was correct, the potential for these fibers to develop high moduli and high thermal conductivities upon similar heat treatment should improve from A to B, and B and C should exhibit similar properties. Of course, all three melt-spun fiber sets must be (and were) oxidized and graphitized in the same manner for such a comparison to be valid.

Table III. Properties of As-Spun and Graphitized Round Fibers Produced from Mesophase M2

Fiber Set	A	B	C
Spin Temperature (°C)	346	351	354
Mesophase Viscosity (Pa.s)	52	36	30
As-Spun Fiber Diameter (μm)	13.7 ± 0.6	13.7 ± 0.6	13.7 ± 0.6
As-Spun Z-value (°)	25.3	23.0	22.9
Graphitized Fiber Diameter (μm)	8.4 ± 0.2	10.5 ± 0.3	11.2 ± 0.3
Graphitized Z-value (°)	17.5	13.8	8.2
L_c (Å)	160	160	200
L_a (Å)	N/A*	330	340
Graphitized d(0002)-spacing (Å)	3.382	3.380	3.379
Tensile Modulus (GPa)	593 ± 30	888 ± 50	810 ± 50
Electrical Resistivity (μΩ-m)	3.7 ± 0.1	3.4 ± 0.3	3.0 ± 0.2

* = The (11$\underline{2}$0) plane of fiber set A was not developed so an L_a value could not be measured.
± = Based upon a 95% confidence interval.

After graphitization at 2400 °C, the graphitized Z-values of the three fiber sets were measured. They follow a similar trend to the as-spun Z-values, with the degree of misorientation of the graphitized fiber decreasing from A to C. As shown in Table III, the crystallite coherence length, L_a, increases from A to B, while B and C have similar values of L_a. The L_a size for A was not reported because it did not develop a $(11\underline{2}0)$ diffraction line upon graphitization as did B and C. This indicates that a-direction crystal growth is poor in A and should be detrimental to transport properties in the a-direction. Because B and C crystallite development in the a-direction was similar, they should possess similar transport capabilities in the a-direction. Additionally, the crystallite stack height, L_c, was significantly larger for C than A or B. Judging from the $d_{(0002)}$-spacing obtained from the (0002) and (0004) diffraction lines, the degree of graphitization increases sequentially from A to B, while B and C have a similarly low $d_{(0002)}$-spacing.
As shown in Table III, the tensile modulus was also determined for the graphitized fibers. As expected from the X-ray data, the modulus of A is significantly lower than those of B and C, which achieved high moduli upon graphitization. This is because the modulus is highly dependent on the degree of basal plane orientation with respect to the fiber axis [9,10].

Because of the strong relationship found to exist between electrical resistivity and thermal conductivity [11], electrical resistivity measurements were made to determine the transport properties of the three fiber sets. As shown in Table III, the electrical resistivity decreases from A to C. As before, this is a result of the increase in preferred orientation, larger L_a size, and smaller interplaner $d_{(0002)}$-spacing that occurs sequentially from A to C [12,13]. Incidentally, the effect of graphitized fiber diameter on our results is believed to be insignificant. The diameters of B and C were identical within statistical limits, and the smaller diameter of A would have improved its properties. Thus, the differences observed between A and B/C are probably conservative.

In summary, the above results indicate that WAXD is an appropriate technique for monitoring the potential of as-spun fibers to yield final high-performance carbon fibers. In addition, higher spinning temperatures, which lead to lower Z-values, result in improved final fiber properties. Finally, it should be noted that the properties obtained for fiber sets B and C are equivalent to those of Amoco's P120, one of the best (and most expensive) carbon fibers produced commercially.

d. Ribbon-Shaped Fibers from Supercritically Extracted Mesophases. In the work described above, round fibers were spun from supercritically extracted mesophases. However, Edie and co-workers [14] have shown that ribbon-shaped fibers exhibit greater potential for improved thermal transport properties. Thus, ribbon-shaped fibers were also evaluated in this project.

Mesophases M1, M2, and M3 (see Tables I and II) were selected for melt spinning. Figure 4 shows the influence of the spinning temperature on the Z-values of "green" fibers melt-spun from M1, M2, and M3. The units of the x-axis were selected to allow one to plot data from mesophases exhibiting different softening points on the same graph. The figure shows how the

orientation of the aromatic layers within the fibers increases with increasing spinning temperature. (At even higher temperatures than those shown here, the mesophase becomes too "watery", and misorientation begins to increase.) Note that this effect was also observed for round carbon fibers spun from mesophases M1 and M2 (see part c above). It should also be noted that, consistent with the results of Edie et al. [14], the Z-values for ribbon-shaped fibers spun from mesophases M1 and M2 were lower than those observed by us for round carbon fibers

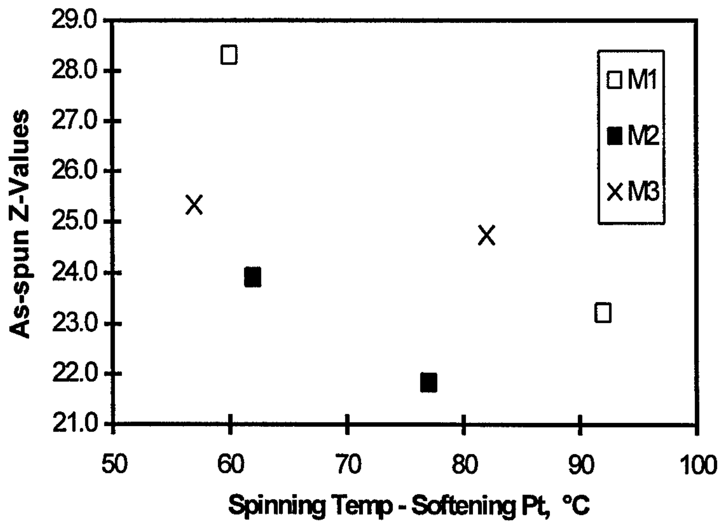

Figure 4. Z-values for ribbon-shaped fibers melt-spun from mesophases M1 through M3.

spun from the same mesophases (compare Table III to Table IV). Mesophases M4 and M5 could not be reproducibly melt-spun into the fiber form because of off-gassing problems, which were accentuated by our use of a batch melt-spinning apparatus. Several factors may have contributed to off-gassing. First, higher spinning temperatures (i.e., 360 °C and up) were required because of the higher softening points of M4 and M5 (see Table II). Such temperatures render any mesophase more susceptible to degradation and the accompanying off-gassing that can occur. Second, M4 had the highest degree of alkyl substitution (see I_{CH} and I_A in Table II) of all mesophases studied. Thus, with larger numbers of alkyl groups present on both the aromatic and naphthenic rings, this mesophase would be expected to be more susceptible to degradation. Third, DRIFTS results indicated that residual toluene was not completely removed from M5 prior to spinning. Because mesophase M6 had such a high softening point (i.e., 323 °C), the melt spinning of this fraction was not attempted.

For each of the three spinnable mesophases, two sets of green ribbon-shaped fibers produced at low and high spinning temperatures (and hence, exhibiting high and low Z-values, respectively) were processed into final carbon fibers. The fiber properties are shown in Table IV. For each mesophase studied, the Z-values of final carbon fibers correlated with the corresponding as-spun Z-values, that is, a decrease in as-spun Z-values resulted, after heat treatment, in a decrease in Z-values within the final fibers. Similarly, the electrical resistivities decreased and the tensile moduli increased with decreasing as-spun Z-values. However, electrical resistivity is related to crystallite size as well as orientation, so the final fibers with the lowest electrical resistivities did not always exhibit the highest tensile moduli. The correlations between Z-values and electrical

resistivities or tensile moduli were confirmed by results for the lattice parameters L_c and L_a, which generally showed an increase in the average crystallite size within the fibers with decreasing Z-values.

Table IV. Properties of As-Spun and Final Ribbon-Shaped Fibers

Mesophase	M1		M2		M3	
Fiber Set	M1-1	M1-2	M2-1	M2-2	M3-1	M3-2
T (°C) [a]	298	330	334	349	331	356
As-Spun Z (°) [b]	28.3	23.2	23.9	21.8	25.3	24.7
Final Z (°) [c]	15.3	10.0	7.6	6.8	10.5	7.2
Area (μm^2)	157	207	216	224	310	380
σ (GPa) [d]	2.26	2.13	2.32	3.13	2.04	1.72
E (GPa) [e]	440	700	420	500	820	850
ρ ($\mu\Omega m$) [f]	4.95	3.26	3.48	3.29	4.71	4.26
d_{002} (Å) [g]	3.384	3.385	3.393	3.392	3.393	3.385
L_c (Å) [h]	133	193	134	110	172	203
L_a (Å) [i]	112	231	384	404	286	280

a Spinning temperature.
b Degree of misorientation (± 0.5).
c Degree of misorientation (± 0.1).
d Tensile strength (±0.2).
e Tensile modulus (±40).
f Electrical resistivity (±0.2).
g d_{002}-spacing.
h Crystallite stack height.
i Crystallite coherence length.

It should be emphasized that comparisons between fiber sets spun from three different supercritically extracted mesophases (which are chemically different) should be made with caution, because heat-treatment conditions for these fibers, which were identical for all sets, have not been optimized. Even so, the results obtained thus far indicate that mesophase M2 would be the preferred precursor for a high thermal conductivity carbon fiber.

In conclusion, an improved degree of preferred orientation with respect to the as-spun fiber axis was observed as the spinning temperature was increased. True statistical differences in the as-spun Z-values of two ribbon-shaped fiber sets spun from the same mesophase yielded, upon identical heat treatment, true statistical differences in tensile properties, electrical resistivities, and crystallographic parameters for the associated fibers. Also, it is important for us to remember that these same trends were observed for round fibers, which gives us confidence in these important conclusions. Thus, X-ray diffraction has been shown to be a useful technique for monitoring the potential of noncircular as-spun fibers to yield final fibers with improved tensile moduli and transport properties.

Finally, even though oxidation conditions were not optimized and the graphitization temperature was only 2400 °C (commercial temperatures can exceed 3000 °C), final fibers with thermal conductivities equal to those exhibited by Amoco's P-120 fibers (i.e., M1-2 and M2-2) were produced. Furthermore, the tensile modulus (E) exhibited by M3-2 is equal to that of the best fibers that are commercially available. Clearly, even unoptimized mesophases produced by supercritical extraction are superior to the mesophases used by Amoco.

e. Mesophase Production by Supercritical Extraction: A Preliminary Economic Analysis. In the Spring of 1997, Prof. Thies taught the capstone design class (i.e., ChE 432) in the Chemical Engineering Curriculum at Clemson University. The design problem for his class was as follows: determine the cost in \$/kg of producing 1 million kg/yr of mesophase pitch by (1) supercritical extraction and by (2) catalytic polymerization of naphthalene (which is the basis for Mitsubishi's process). Six four-man groups worked on this design problem during the semester under the supervision of Prof. Thies, putting in 15-20 hr/person/wk. Thus, their results can be regarded as a good first estimate of the costs of producing these mesophases. General assumptions that were made by all groups included a discounted cash flow analysis, a 20% return on investment (ROI), and a plant life of 10 years.

Key results of the economic analysis are as follows:

- The continuous nature of the supercritical extraction process is a significant advantage, and the costs associated with the higher pressures inherent in the process can be minimized by using heat exchangers to cool streams back to the liquid state before pumping (vs. compressing them as supercritical fluids).
- The batch nature of the AR process increases its costs significantly. In addition, the AR process requires very expensive Hastelloy C reactors for the HF/BF_3 catalyst. Compression and recovery of the volatile catalyst is also expensive, and removal of the isotropic oils in the AR mesophase is difficult.
- To obtain the same ROI, the supercritically extracted mesophase must be sold for \$3.75±1.00/kg, and the AR mesophase must be sold for \$6.75±1.00/kg. (Incidentally, \$6.75/kg agrees closely with the current selling price of AR mesophase, which is more than \$7/kg.)

Thus, the conclusion of this preliminary design analysis is that producing mesophase by supercritical extraction is economically feasible.

6. List of Publications and Technical Reports

Refereed Journals

a. Dauché, F. M., Barnes, A. B., Gallego, N. C., Edie, D. D., and Thies, M. C., "Ribbon-Shaped Carbon Fibers from Supercritically Extracted Mesophase Pitches," Carbon, **36,** 1238 (1998).

b. Dauché, F. M., Bolaños, G., Blasig, A., and Thies, M. C., "Control of Mesophase Pitch Properties by Supercritical Fluid Extraction," Carbon, **36,** 953 (1998).

c. Barnes, A. B., Dauché, F. M., Gallego, N. C., Fain, C. C., and Thies, M. C., "As-spun Orientation as an Indication of Graphitized Properties of Mesophase-Based Carbon Fiber", Carbon, **36,** 855 (1998).

d. Fleurot, O., and Edie, D. D. "Steady and Transient Rheological Behavior of Mesophase Pitches." Journal of Rheology, **42** (4), 825 (1998).

e. Bolaños, G. and Thies, M. C., "Supercritical Toluene-Petroleum Pitch Mixtures: Liquid-Liquid Equilibria and SAFT Modeling," Fluid Phase Equilibria, **117**, 273 (1996).

Conference Proceedings

a. Dauche, F.M., A.B. Barnes, N.C. Gallego, C.C. Fain, D.D. Edie, and M.C. Thies, "High Thermal Conductivity Carbon Fibers From Supercritically Extracted Mesophase Pitch", **Carbon '97**, Proceedings of the 23rd Biennial Conference on Carbon, Penn State U., PA, July 1997, Vol II, p. 436.

b. Fleurot, O. and D. D. Edie, "Modeling of Structure Development During Flow of Mesophase Pitch Through Capillaries," **Carbon '97**, Proceedings of the 23rd Biennial Conference on Carbon, Penn State U., PA, July 1997, Vol. II, p. 416.

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7. List of all Participating Scientific Personnel Supported by this Project

Faculty: M. C. Thies, D. D. Edie, C. C. Fain, and J. N. Beard

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Degrees Received While Employed on the Project:
Ph.D.

1. G. Bolanos, "Production of Mesophase Pitch by Supercritical Fluid Extraction: A Study of the Region of Liquid-Liquid Equilibrium", May 1995.

2. Franck M. Dauche, "High Performance Carbon Fibers from Mesophases Produced by SCF Extraction", December 1997.

3. Olivier Fleurot, "The Viscoelastic Flow Behavior of Pitches", May 1998.

M.S.

1. A.C. Geiculescu, "Preparation of Petroleum Pitch Pseudocomponents by Gel Permeation Chromatography", August 1994.

2. C. Kilander, "Computer Control of a Pilot-Scale Supercritical Fluid Extraction Apparatus", August 1995.

3. Andre Blasig, "Production of Mesophase Pitch by Supercritical Fluid Extraction: An Exploration of the Operating Conditions" April 1996.

4. Nidia Gallego, "Characterization of Fibers Produced from SCF-Extracted Mesophase", December 1996.

5. Allan B. Barnes, "Heat Treatment and Structural Evaluation of SCF-Extracted Mesophase-Based Carbon Fibers" August 1997.

6. Philip Meinkoehn, "Fractionation of Petroleum Pitches with Near Critical and Supercritical Fluids" August 1997.

8. Report of Inventions: None

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10. Appendices: None